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CHEMISTRY
HIGHER LEVEL
PAPER 2

Candidate session number

Monday 19 May 2014 (afternoon)

2 hours 15 minutes

Examination code

2	2	1	4	–	6	1	1	4

INSTRUCTIONS TO CANDIDATES

- Write your session number in the boxes above.
- Do not open this examination paper until instructed to do so.
- Section A: answer all questions.
- Section B: answer two questions.
- Write your answers in the boxes provided.
- A calculator is required for this paper.
- A clean copy of the ***Chemistry*** *Data Booklet* is required for this paper.
- The maximum mark for this examination paper is *[90 marks]*.

33 pages

SECTION A

*Answer **all** questions. Write your answers in the boxes provided.*

1. A class studied the equilibrium established when ethanoic acid and ethanol react together in the presence of a strong acid, using propanone as an inert solvent. The equation is given below.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

One group made the following **initial mixture**:

Liquid	**Volume / cm^3**
Ethanoic acid	5.00 ± 0.05
Ethanol	5.00 ± 0.05
$6.00\,mol\,dm^{-3}$ aqueous hydrochloric acid	1.00 ± 0.02
Propanone	39.0 ± 0.5

(a) The density of ethanoic acid is $1.05\,g\,cm^{-3}$. Determine the amount, in mol, of ethanoic acid present in the initial mixture. *[3]*

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(Question 1 continued)

(b) The concentration of ethanoic acid can be calculated as $1.748\,\text{mol}\,\text{dm}^{-3}$. Determine the percentage uncertainty of this value. (Neglect any uncertainty in the density and the molar mass.) *[3]*

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(c) After one week, a $5.00 \pm 0.05\,\text{cm}^3$ sample of the final equilibrium mixture was pipetted out and titrated with $0.200\,\text{mol}\,\text{dm}^{-3}$ aqueous sodium hydroxide to determine the amount of ethanoic acid remaining. The following titration results were obtained:

Titration number	1	2	3
Initial reading / $\text{cm}^3 \pm 0.05$	1.20	0.60	14.60
Final reading / $\text{cm}^3 \pm 0.05$	28.80	26.50	40.70
Titre / cm^3	27.60	25.90	26.10

(i) Calculate the absolute uncertainty of the titre for Titration 1 ($27.60\,\text{cm}^3$). *[1]*

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(This question continues on the following page)

(Question 1 continued)

(ii) Suggest the average volume of alkali, required to neutralize the $5.00\,cm^3$ sample, that the student should use. *[1]*

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(iii) $3.00\,cm^3$ of the $0.200\,mol\,dm^{-3}$ aqueous sodium hydroxide reacted with the hydrochloric acid present in the $5.00\,cm^3$ sample. Determine the concentration of ethanoic acid in the final equilibrium mixture. *[2]*

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(iv) Deduce the equilibrium constant expression for the reaction. *[1]*

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(Question 1 continued)

(v) The other concentrations in the equilibrium mixture were calculated as follows:

Compound	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
Concentration / mol dm^{-3}	0.884	0.828	1.80

Use these data, along with your answer to part (iii), to determine the value of the equilibrium constant. (If you did not obtain an answer to part (iii), assume the concentrations of ethanol and ethanoic acid are equal, although this is not the case.) *[1]*

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(d) Outline how you could establish that the system had reached equilibrium at the end of one week. *[1]*

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(e) Outline why changing the temperature has only a very small effect on the value of the equilibrium constant for this equilibrium. *[1]*

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(This question continues on the following page)

(Question 1 continued)

(f) Outline how adding some ethyl ethanoate to the initial mixture would affect the amount of ethanoic acid converted to product. *[2]*

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(g) Propanone is used as the solvent because one compound involved in the equilibrium is insoluble in water. Identify this compound and explain why it is insoluble in water. *[2]*

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(h) Suggest **one** other reason why using water as a solvent would make the experiment less successful. *[1]*

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2. There are only two isotopes, ${}^{63}_{29}Cu$ and ${}^{65}_{29}Cu$, in naturally occurring copper.

(a) The relative atomic mass of copper is 63.55. Calculate the percentage of ${}^{63}_{29}Cu$ in the naturally occurring element. *[2]*

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(b) State the **full** electronic configuration of a copper atom. *[1]*

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(c) Explain why most copper(II) compounds are coloured, whereas most copper(I) compounds are not. *[2]*

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(Question 2 continued)

(d) A chemist considered preparing a copper(I) salt by reacting copper metal with the corresponding copper(II) salt according to the equation below.

$$Cu^{2+}(aq) + Cu(s) \rightarrow 2Cu^{+}(aq)$$

(i) Using data from Table 14 of the Data Booklet, calculate the cell potential for this reaction. *[2]*

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(ii) Use this result to predict, with a reason, whether this reaction will be spontaneous. *[1]*

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3. The reaction between 2-bromopropane and potassium hydroxide can produce two different organic products, depending on the conditions. State the name of each organic product and outline the conditions needed to give a high yield of each product. *[6]*

	Product 1	**Product 2**
Name	. . . .	. . . .
Conditions	. . . .	. . . .

4. Ozone, O_3, in the upper atmosphere prevents harmful UV radiation reaching the surface of the Earth.

(a) Draw the Lewis structure for ozone. *[1]*

(b) State the shape of the ozone molecule and estimate the bond angle. *[2]*

Shape:

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Bond angle:

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(c) State the hybridization of the central oxygen atom. *[1]*

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(d) In terms of σ and π bonds, describe the two oxygen-oxygen bonds in the Lewis structure. *[1]*

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(This question continues on the following page)

(Question 4 continued)

(e) The two oxygen-oxygen bonds in ozone are in fact of equal length. Deduce why this is the case and how the length of these would compare to oxygen-oxygen bond lengths in hydrogen peroxide, H_2O_2, and in the oxygen molecule, O_2. *[2]*

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SECTION B

*Answer **two** questions. Write your answers in the boxes provided.*

5. Bleaches in which chlorine is the active ingredient are the most common, although some environmental groups have concerns about their use.

(a) (i) Describe the colour change that occurs when aqueous chlorine is added to aqueous sodium bromide. *[1]*

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(ii) Outline, with the help of a chemical equation, why this reaction occurs. *[2]*

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(b) In aqueous chlorine the equilibrium below produces chloric(I) acid (hypochlorous acid), HOCl, the active bleach.

$$Cl_2(aq) + H_2O(l) \rightleftharpoons HOCl(aq) + H^+(aq) + Cl^-(aq)$$

(i) Chloric(I) acid is a weak acid, but hydrochloric acid is a strong acid. Outline how this is indicated in the equation above. *[1]*

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(Question 5 continued)

(ii) State a balanced equation for the reaction of chloric(I) acid with water. *[1]*

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(iii) Outline, in terms of the equilibrium in aqueous chlorine, why it is dangerous to use an acidic toilet cleaner in combination with this kind of bleach. *[2]*

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(iv) Suggest why a covalent molecule, such as chloric(I) acid, is readily soluble in water. *[2]*

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(Question 5 continued)

(v) Partial neutralization of chloric(I) acid creates a buffer solution. Given that the pK_a of chloric(I) acid is 7.53, determine the pH of a solution that has $[HOCl] = 0.100\ mol\ dm^{-3}$ and $[ClO^{-}] = 0.0500\ mol\ dm^{-3}$. *[4]*

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(vi) Describe, using HIn to represent the indicator in its acid form, why an indicator changes colour when excess alkali is added. *[3]*

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(Question 5 continued)

(c) Aqueous sodium chlorate(I), NaOCl, the most common active ingredient in chlorine based bleaches, oxidizes coloured materials to colourless products while being reduced to the chloride ion. It will also oxidize sulfur dioxide to the sulfate ion.

(i) Deduce a balanced equation for the reaction between the chlorate(I) ion and sulfur dioxide from the appropriate half-equations. *[4]*

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(ii) State the initial and final oxidation numbers of both chlorine and sulfur in the final equation. *[2]*

Element	**Initial oxidation number**	**Final oxidation number**
Chlorine		
Sulfur		

(d) The standard electrode potential for the reduction of the chlorate(V) ion to the chloride ion is +1.49 V.

(i) Define the term *standard electrode potential*. *[1]*

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(This question continues on the following page)

(Question 5 continued)

(ii) Referring to Table 14 of the Data Booklet, deduce, giving a reason, whether the oxidation of the chromium(III) ion to the dichromate(VI) ion by the chlorate(V) ion is energetically feasible. *[2]*

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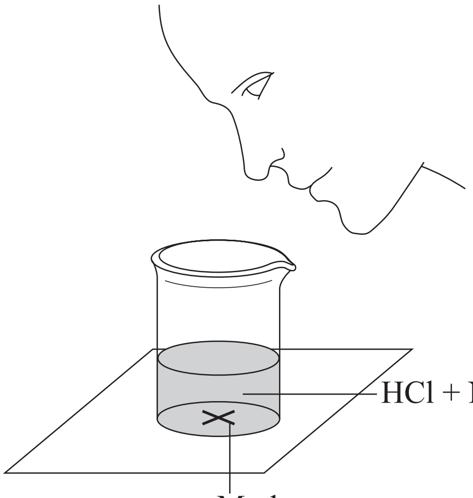
6. A group of students investigated the rate of the reaction between aqueous sodium thiosulfate and hydrochloric acid according to the equation below.

$$Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + SO_2(g) + S(s) + H_2O(l)$$

The two reagents were rapidly mixed together in a beaker and placed over a mark on a piece of paper. The time taken for the precipitate of sulfur to obscure the mark when viewed through the reaction mixture was recorded.



Initially they measured out $10.0\,cm^3$ of $0.500\,mol\,dm^{-3}$ hydrochloric acid and then added $40.0\,cm^3$ of $0.0200\,mol\,dm^{-3}$ aqueous sodium thiosulfate. The mark on the paper was obscured 47 seconds after the solutions were mixed.

(a) The teacher asked the students to measure the effect of halving the concentration of sodium thiosulfate on the rate of reaction.

(i) State the volumes of the liquids that should be mixed. *[1]*

Liquid	$0.500\,mol\,dm^{-3}$ HCl	$0.0200\,mol\,dm^{-3}$ $Na_2S_2O_3$	Water
Volume / cm^3			

(ii) State why it is important that the students use a similar beaker for both reactions. *[1]*

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(This question continues on the following page)

(Question 6 continued)

(iii) If the reaction were first order with respect to the thiosulfate ion, predict the time it would take for the mark on the paper to be obscured when the concentration of sodium thiosulfate solution is halved. *[1]*

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(b) One proposed mechanism for this reaction is:

$$S_2O_3^{2-}(aq) + H^+(aq) \rightleftharpoons HS_2O_3^-(aq) \qquad \textit{Fast}$$

$$HS_2O_3^-(aq) + H^+(aq) \rightarrow SO_2(g) + S(s) + H_2O(l) \qquad \textit{Slow}$$

(i) Deduce the rate expression of this mechanism. *[1]*

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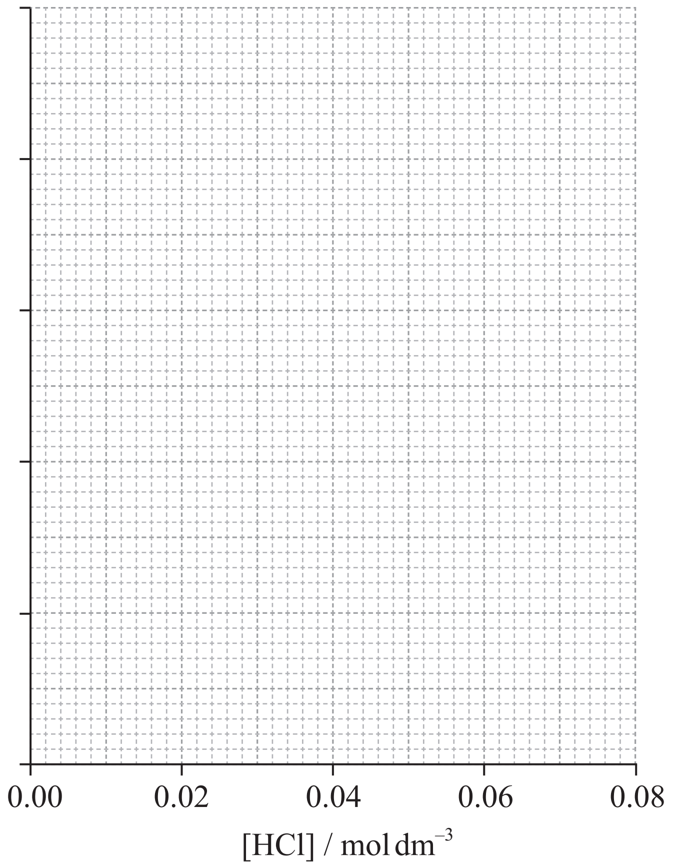
(Question 6 continued)

(ii) The results of an experiment investigating the effect of the concentration of hydrochloric acid on the rate, while keeping the concentration of thiosulfate at the original value, are given in the table below.

[HCl] / mol dm^{-3}	0.020	0.040	0.060	0.080
Time / s	89.1	72.8	62.4	54.2

On the axes provided, draw an appropriate graph to investigate the order of the reaction with respect to hydrochloric acid. *[3]*



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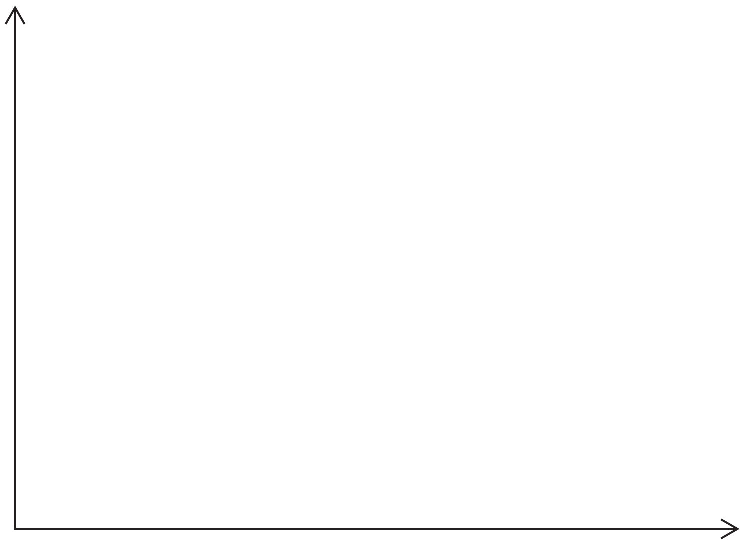
(Question 6 continued)

(iii) Identify **two** ways in which these data **do not** support the rate expression deduced in part (i). *[2]*

(c) (i) Sketch and label, indicating an approximate activation energy, the Maxwell–Boltzmann energy distribution curves for two temperatures, T_1 and T_2 ($T_2 > T_1$), at which the rate of reaction would be significantly different. *[3]*



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(Question 6 continued)

(ii) Explain why increasing the temperature of the reaction mixture would significantly increase the rate of the reaction. *[3]*

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(d) The teacher asked the students to devise another technique to measure the rate of this reaction.

(i) One group suggested recording how long it takes for the pH of the solution to change by one unit. Calculate the initial pH of the original reaction mixture. *[2]*

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(ii) Deduce the percentage of hydrochloric acid that would have to be used up for the pH to change by one unit. *[1]*

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(Question 6 continued)

(e) Another group suggested collecting the sulfur dioxide and drawing a graph of the volume of gas against time.

(i) Calculate the volume of sulfur dioxide, in cm^3, that the original reaction mixture would produce if it were collected at 1.00×10^5 Pa and 300 K. *[3]*

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(ii) Sulfur dioxide, a major cause of acid rain, is quite soluble in water and the equilibrium shown below is established.

$$SO_2(aq) + H_2O(l) \rightleftharpoons HSO_3^-(aq) + H^+(aq)$$

Given that the K_a for this equilibrium is $1.25 \times 10^{-2}\,mol\,dm^{-3}$, determine the pH of a $2.00\,mol\,dm^{-3}$ solution of sulfur dioxide. *[3]*

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(iii) Using Table 15 of the Data Booklet, identify an organic acid that is a stronger acid than sulfur dioxide. *[1]*

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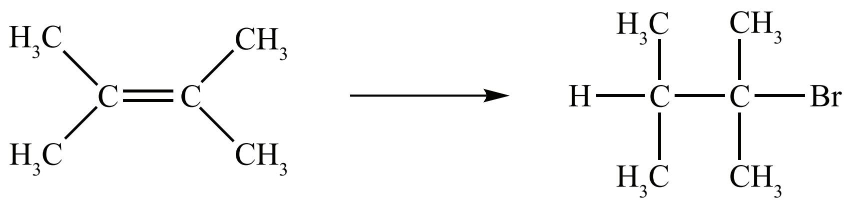
7. Alkenes, such as **A** (shown below), are important intermediates in the petrochemical industry because they undergo addition reactions to produce a wide variety of products, such as the conversion shown below.



A **B**

(a) State the reagent required to convert **A** into **B**. *[1]*

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(b) It is also possible to convert **B** into **A**. Explain the mechanism of this reaction using curly arrows to represent the movement of electron pairs. *[4]*

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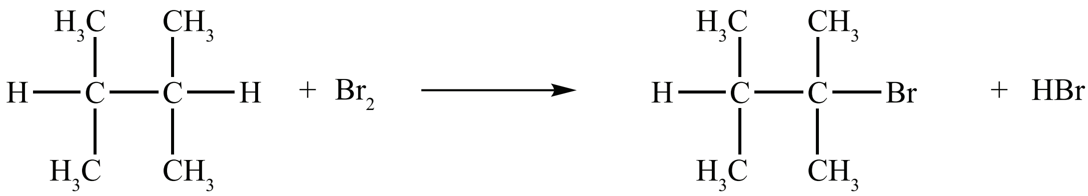
(Question 7 continued)

(c) Another way to make **B** is the reaction shown below.



(i) State the conditions required for this reaction to occur. *[1]*

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(ii) Outline why it would give a poor yield of the desired product. *[1]*

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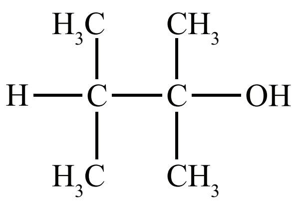
(d) **B** can be converted into **C**.



C

(i) State the reagent required. *[1]*

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(Question 7 continued)

(ii) State the rate expression that you would expect for the conversion of **B** to **C**. *[1]*

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(iii) Explain why **C** would **not** be optically active. *[2]*

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(iv) State why **C** is not readily oxidized by acidified potassium dichromate(VI). *[1]*

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(v) Deduce the structural formula of an isomer of **C** that would be optically active and could also be oxidized to a carboxylic acid by acidified potassium dichromate(VI). *[2]*

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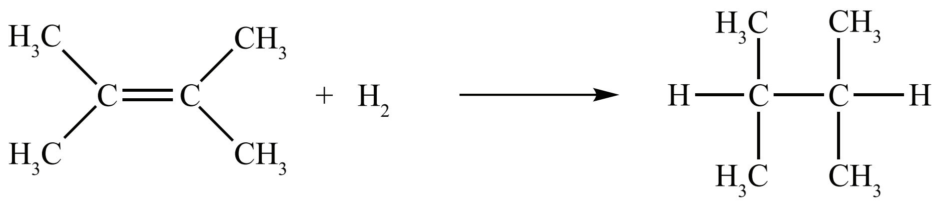
(Question 7 continued)

(e) In the gas phase, **A** reacts with hydrogen to form **D**:



A **D**

(i) State the conditions required for this reaction to occur. *[1]*

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(ii) Outline a use for hydrogenation reactions like this in the manufacture of foodstuffs. *[1]*

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(iii) State, with a reason, whether you would expect the entropy change for this reaction to be positive or negative. *[1]*

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(This question continues on the following page)

(Question 7 continued)

(iv) Given that the enthalpy change of formation of compounds **A** and **D**, in the gas phase, is $-68\,kJ\,mol^{-1}$ and $-178\,kJ\,mol^{-1}$, respectively, calculate the enthalpy change for the reaction of **A** with hydrogen. *[2]*

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(v) Explain how the spontaneity of this reaction would depend on the temperature at which it was carried out. *[2]*

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(vi) The standard enthalpy change of combustion of **A** is $-4000\,kJ\,mol^{-1}$. Calculate the amount of **A**, in mol, that would have to be burned to raise the temperature of $1\,dm^3$ of water from 20 °C to 100 °C. *[2]*

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(Question 7 continued)

(vii) Compound **D** is isomeric with hexane. Predict, giving reasons, how the boiling points of these compounds would compare. *[2]*

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8. Magnesium, a reactive metal found in many common minerals, is also an essential nutrient for both plants and animals.

(a) Define the term *first ionization energy*. *[2]*

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(b) Successive ionization energies of magnesium are given in the table below.

	First	**Second**	**Third**
Energy required / kJ mol^{-1}	738	1450	7730

(i) Explain why the second ionization energy is greater than the first ionization energy. *[2]*

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(ii) Explain why the third ionization energy is **much** greater than the second ionization energy. *[2]*

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(Question 8 continued)

(c) Although magnesium is usually found as Mg^{2+} in its compounds, it is possible to use the Born–Haber cycle to investigate the possibility of Mg^{+} being able to form stable compounds.

Use the ionization energy data from part (b), along with the other data provided below, to determine the enthalpy change of formation of MgCl(s). Assume that, because Mg^{+} would be similar in size to Na^{+}, MgCl would have a similar lattice enthalpy to NaCl.

Enthalpy of atomization of Mg	+146 kJ mol^{-1}
Bond enthalpy in Cl_2	+243 kJ mol^{-1}
Electron affinity of Cl	–349 kJ mol^{-1}
Lattice enthalpy of NaCl	+790 kJ mol^{-1}

[3]

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(d) Consider the lattice enthalpies of MgF_2, $MgCl_2$ and $CaCl_2$. List these from the most endothermic to the least endothermic and explain your order. *[3]*

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Most endothermic ⟶ Least endothermic

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(Question 8 continued)

(e) Magnesium hydroxide, $Mg(OH)_2$, is only sparingly soluble in water and the equilibrium below exists when excess solid is in contact with a saturated solution.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

Outline how the solubility of magnesium hydroxide will vary with pH. *[2]*

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(f) Magnesium metal is mainly used as a component in lightweight alloys, particularly in combination with aluminium and titanium.

(i) Describe the bonding present in magnesium metal. *[2]*

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(ii) Suggest why magnesium is harder than sodium. *[1]*

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(This question continues on the following page)

(Question 8 continued)

(iii) Outline why alloys are generally less malleable than their component metals. *[1]*

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(g) Magnesium is usually produced by the electrolysis of molten magnesium chloride.

(i) Draw a labelled diagram of a suitable apparatus for the electrolysis. *[2]*

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(Question 8 continued)

(ii) State equations for the reactions that take place at the electrodes. *[2]*

Negative electrode (cathode) reaction:

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Positive electrode (anode) reaction:

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(iii) When **dilute** aqueous magnesium chloride is used as the electrolyte, the reactions at both electrodes are different. State equations for the reactions that occur in aqueous solution. *[2]*

Negative electrode (cathode) reaction:

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Positive electrode (anode) reaction:

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(iv) Outline why magnesium metal is not produced in the electrolysis of aqueous magnesium chloride. *[1]*

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